Non-stabilized azomethine ylides in [3 + 2] cycloadditions. Pyrrolidinylfuranones from (5*S*)-5-menthyloxy-4-vinylfuran-2(5*H*)-one

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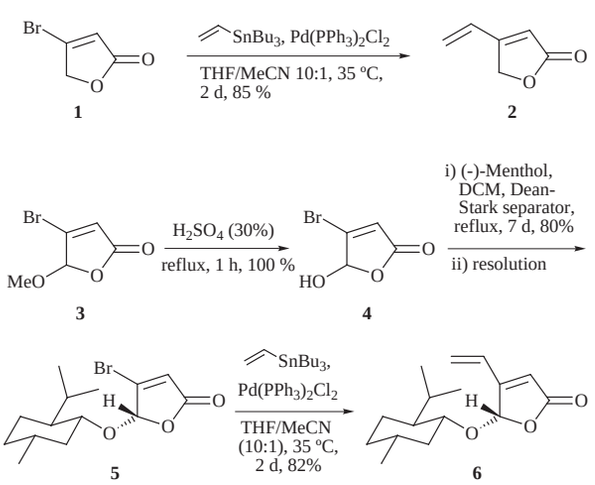
Upon sonication with lithium fluoride in acetonitrile *N*-benzyl-*N*-methoxymethyl(trimethylsilylmethyl)amines **9a–c** undergo chemoselective 1,3-dipolar cycloaddition with 4-vinylfuranones **2** and **6** to afford pyrrolidinylfuranones **10**, **11a–c** and **12a–c**. The stereochemistry is assigned by X-ray analyses and proton NMR data comparison of related oxiranylfuranone **13**.

4-Vinylfuran-2(5*H*)-ones, which have received little attention hitherto, are well suited for the construction of heteroprostanoids containing a pyrrolidine ring and also other heterocycles, which are attached to an electron-deficient butenolide moiety.

We here describe the synthesis of (5*S*)-5-menthyloxy-4-vinylfuran-2(5*H*)-one **6**. Heterocycle **6** was obtained enantiomerically pure and is useful for elucidating the stereochemistry of simple [2 + 3] and [2+ 1] cycloadditions to the vinyl group. Carbon C-5 of the furan-2(5*H*)-one possesses an oxygenated side-chain, as in simple derivatives and metabolites of 4-vinylfuran-2(5*H*)-one **2**.

Results

The synthesis of (5*S*)-5-menthyloxy-4-vinylfuran-2(5*H*)-one **6** is described in Scheme 1. We had earlier reported the direct



Scheme 1 Synthesis of the dipolarophiles.

transacetalization of 4-bromo-5-methoxyfuran-2(5*H*)-one **3** with various alcohols in the melt.[1] We now find that it is preferable to carry out this conversion in two steps. Under forcing conditions (30% H_2SO_4) methoxy acetal **3** was first of all converted into hemiacetal **4** in quantitative yield.[2] The subsequent acetalization (**4** ⟶ **5**) proceeded in much milder conditions, *i.e.* refluxing DCM with removal of the water liberated. In contrast, refluxing **4** in toluene under acid catalysis (PTSA) caused

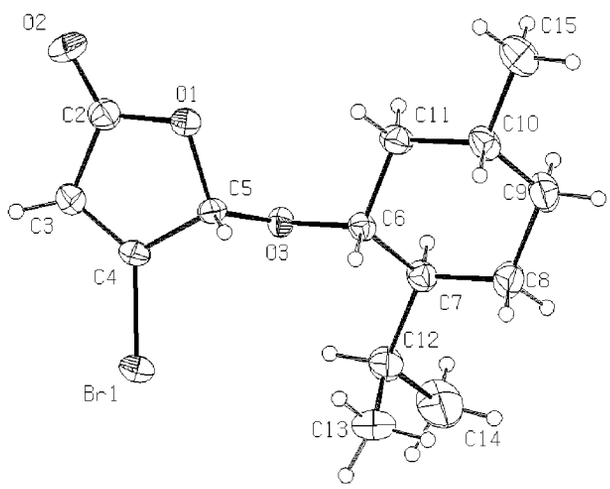


Fig. 1 X-Ray structure of (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one **5**.

a severe drop in yield.[3] We obtained the epimers of **5** in a ratio of (5*S*)-**5**:(5*R*)-**5** = 1.25:1. MM2 calculations suggest that the major (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one **5** is more stable (by *ca.* 2 kcal mol^{-1}) than its diastereomer.[4] A simple recrystallization from petroleum ether–diethyl ether mixtures furnished enantiomerically pure (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one **5**, the structure of which was determined by X-ray crystal diffraction (Fig. 1).[5] The diastereomer of **5** (with respect to carbon C-5) was recycled to 4-bromo-5-hydroxyfuran-2(5*H*)-one **4** by acidic hydrolysis.

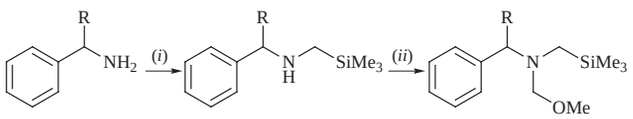
Stille reaction with tributylvinylstannane gave cross-coupled **6** in good yield (82%). Similarly 4-vinylfuran-2(5*H*)-one **2** was prepared readily from tetronic acid bromide **1** (yield 85%), no doubt due to the activation of the carbon–bromine bond by the vinylogous lactone carbonyl group.

The synthesis of the azomethine ylide precursors **9a–c** required two steps. Benzylamines **7a–c** were treated with trimethylsilylmethyl chloride using potassium carbonate in refluxing acetonitrile to give the α-aminosilanes **8a–c** in good yield (Scheme 2). Subsequent reaction with methanolic 40% aqueous formaldehyde afforded the tertiary amines **9a–c** in satisfactory yield and set the stage for the fluoride mediated 1,3-dipolar cycloadditions.[6,7]

Parent vinylfuranone **2** was converted into pyrrolidinyl-

Table 1 Reaction of vinylfuranone **6** with amines **9a–c**

Entry	Dipole precursor 9	R	Conditions	Products 11/12	Yield (%)	ratio 11:12
1	**b**	(*R*)-Me	−40 °C, MeCN/THF	**b**	55	2:1
2	**c**	(*S*)-Me	−40 °C, MeCN/THF	**c**	39	2.92:1
3	**a**	H	0 °C, sonication, 8 h	**a**	73	2.5:1
4	**b**	(*R*)-Me	0 °C, sonication, 8 h	**b**	88	2:1
5	**b**	(*R*)-Me	0 °C, sonication, cat. $Eu(fod)_3$, 8 h	**b**	74	2.45:1
6	**c**	(*S*)-Me	0 °C, sonication, 8 h	**c**	69	3.2:1

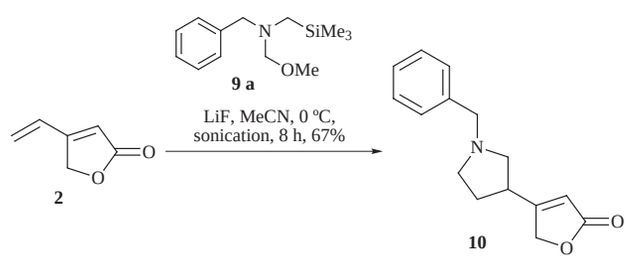


7a–c **8a–c** **9a–c**

	7	R	8	Yield (%)	9	Yield (%)
1	**a**	H	**a**	80	**a**	55
2	**b**	(*R*)-Me	**b**	81	**b**	64
3	**c**	(*S*)-Me	**c**	75	**c**	69

Scheme 2 Synthesis of azomethine ylide precursors. *Reagents and conditions:* (*i*) Me_3SiCH_2Cl, K_2CO_3, MeCN, reflux, 4 d; (*ii*) $CH_2O_{(aq.)}$, K_2CO_3, MeOH, 0 °C, 2.5 h.

furanone **10** by cycloaddition of the azomethine ylide generated *in situ* from **9a** using lithium fluoride (Scheme 3). This test reac-



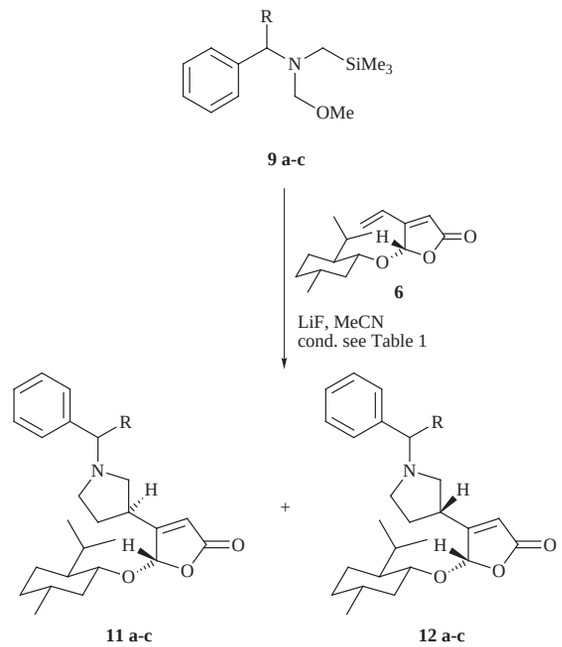
Scheme 3

tion showed that it was possible to combine the electron-rich amine with the oxacyclic Michael acceptor. We were pleased to find that menthyloxy derivative **6** reacted similarly (Scheme 4). Cycloaddition occurred exclusively at the more accessible terminal olefinic bond. The more hindered C3–C4 double bond, although potentially more electron-deficient, was not attacked.[8]

Because of the poor solubility of lithium fluoride in acetonitrile, sonication at 0 °C (bp of acetonitrile 81 °C) was helpful.[9] This also applied to the reactions with enantiopure vinylfuranone **6**, which were carried out without sonication at −40 °C in mixed solvent (acetonitrile–THF) and again with sonication at 0 °C (Table 1). Lowering the temperature to −40 °C had no noticeable effect on the diastereoselectivity of the cycloaddition, while addition of the mild Lewis acid $Eu(fod)_3$ changed the diastereoselectivity slightly (from 2:1 to 2.45:1).[10] Reaction of (1*S*)-*N*-phenylethyl-*N*-methoxymethyl-(trimethylsilylmethyl)amine **9c** with vinylfuranone **6** gave the best diastereomeric ratio (Entry 6) possibly as a consequence of double asymmetric induction.[11]

The diasteromeric pyrrolidinylfuranones were separated by medium pressure liquid chromatography.

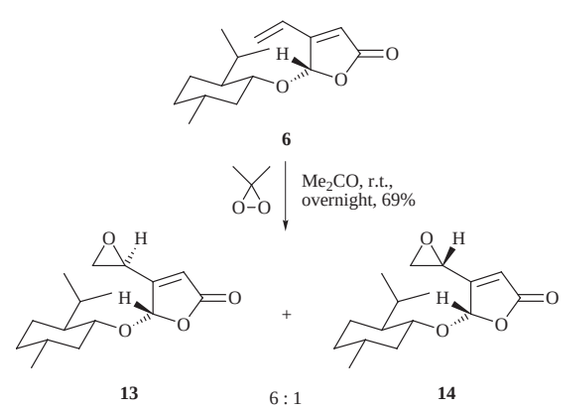
The stereochemistry of pyrrolidinylfuranones **11a–c** and **12a–c** could not easily be determined by common NMR spectroscopic methods. Investigation of the diastereomeric mixtures by proton spectroscopy showed two sets of protons H-3 and H-5, with characteristic chemical shift differences and characteristic relative positions in each case (*cf.* Fig. 2, spectrum C).



Scheme 4 Syntheses of pyrrolidinylfuranones.

The position and multiplicity of the new tertiary proton gave no satisfactory stereochemical information.

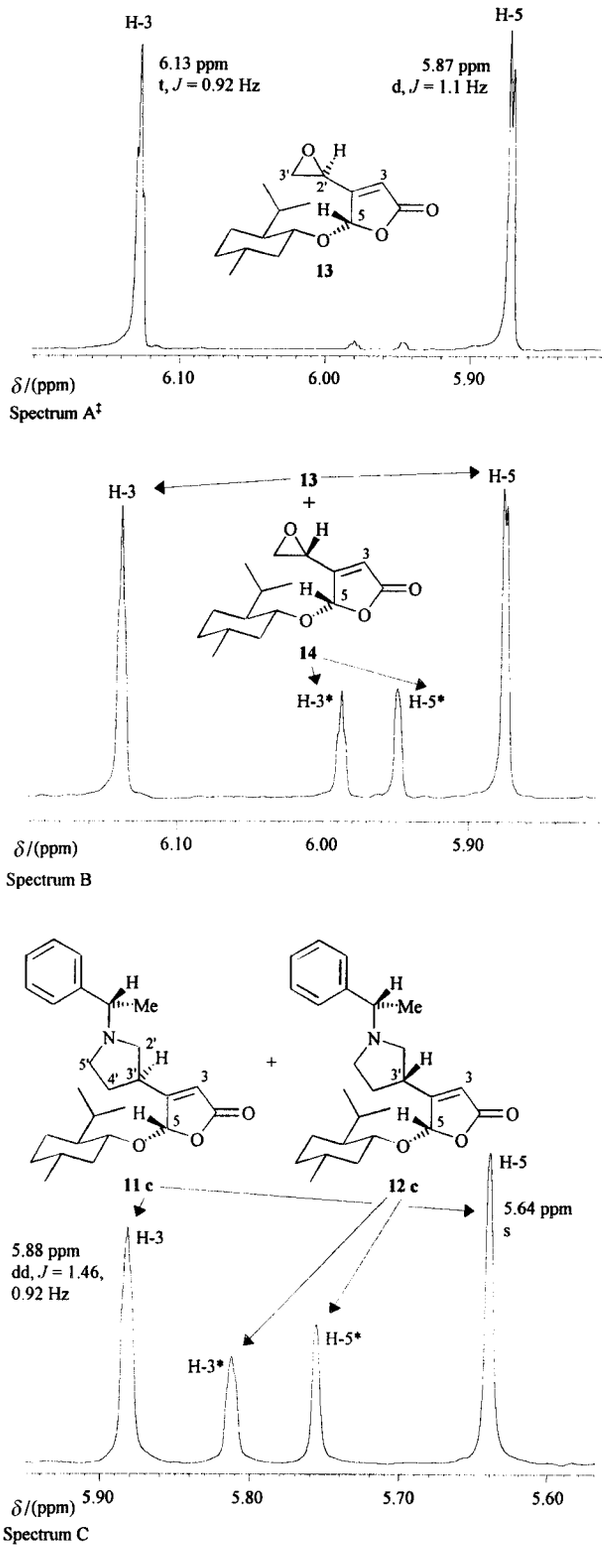
However, epoxidation of (5*S*)-5-menthyloxy-4-vinylfuran-2(5*H*)-one **6** with dimethyldioxirane in acetone furnished the crystalline diastereomeric epoxides **13** and **14** under mild conditions (69% yield, 71% diastereoselectivity, Scheme 5).[12]



Scheme 5 Epoxidation of vinylfuranone **6**.

Major oxiranylfuranone **13** was separated and purified twice by recrystallization. X-Ray crystallography[5] (Fig. 3) showed the configuration of the new chiral centre to be *S*.

The relative positions of the furanone ^1H absorptions of epoxides **13** and **14** were similar to those of the diastereomeric pyrrolidinylfuranones **11c** and **12c** (*cf.* spectra A, B and C). Thus it appears that the relative and also absolute configuration of the title heterocycles **11a–c** and **12a–c** can be determined by



‡The two coupling constants agree within experimental error

Fig. 2

simply comparing the proton NMR data with those of oxiranylfuranones **13** and **14**.

Conclusion

We have prepared novel bicyclic conjugates by combining protected and electron-rich pyrrolidines with an oxacyclic Michael acceptor by a σ-bond at carbon atoms C-3′ and C-4, respectively. These conjugates are potential heteroprostanoids and are of interest as low molecular weight bioregulators.

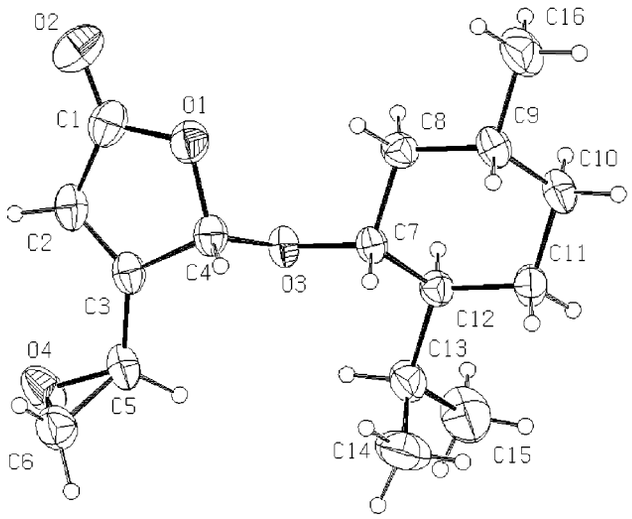


Fig. 3 X-Ray structure of (5*S*)-5-menthyloxy-4-[(2*S*)-oxiran-2-yl]-furan-2(5*H*)-one **13**.

Experimental

General

Melting points were determined on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 infrared spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker WH 90, AM 200 and AM 400 spectrometer in deuterated chloroform unless otherwise stated, with tetramethylsilane as internal standard. Coupling constants, *J*, are given in Hz. Mass spectra were recorded on a Finnigan MAT312 (70 eV) or a VG Autospec spectrometer. Microanalyses were performed in the Department of Organic Chemistry of the University of Hannover. Preparative column chromatography was performed on J. T. Baker silica gel (particle size 30–60 mm). Analytical TLC was carried out on aluminum-backed 0.2 mm silica gel 60 F_{254} plates (E. Merck).

Preparation of 4-bromofuran-2(5*H*)-one **1**, 4-vinylfuran-2(5*H*)-one **2** and 4-bromo-5-methoxyfuran-2(5*H*)-one **3** was described previously.[1]

4-Bromo-5-hydroxyfuran-2(5*H*)-one 4 and (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one 5

4-Bromo-5-methoxyfuran-2(5*H*)-one **3** (1.93 g, 10 mmol) was heated at reflux for 1 h in 30% aqueous sulfuric acid (60 cm^3). The mixture was poured onto ice and extracted with diethyl ether (3×). The combined organic layers were freed from solvent to give 4-bromo-5-hydroxyfuran-2(5*H*)-one **4** as a yellow oil, which was transferred as a solution in DCM (30 cm^3) into a two-necked flask equipped with a Dean–Stark separator. (−)-Menthol (2.5 g, 1.6 eq.) was added and the mixture was refluxed for one week. Evaporation of the solvent and column chromatography (silica gel, petroleum ether–diethyl ether 10:1) afforded 4-bromo-5-menthyloxyfuran-2(5*H*)-one as a mixture of epimers (white crystals, 2.54 g, 8 mmol, 80%, ratio (5*S*)-**5**/(5*R*)-**5** = 1.25:1). Recrystallization from petroleum ether (bp 40–60 °C)–diethyl ether furnished enantiopure (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one **5**.

4-Bromo-5-hydroxyfuran-2(5*H*)-one 4

Crystallization of the crude viscous product from acetone gave white crystals, mp 71 °C; ν_{max}(KBr)/cm^{-1} 3305, 3115, 1717, 1610, 1440, 1333, 1297, 1257, 1184, 1136, 1037, 956, 859, 843, 717; ν_{max}($CHCl_3$)/cm^{-1} 3584, 3120, 3040, 1796, 1768, 1612, 1420, 1320, 1248, 1120, 1032, 960, 892, 864, 840; δ_H(80 MHz; $CDCl_3$; Me_4Si) 2.18 (s, Me_2CO, solvated), 4.65 (1 H, br s, OH), 6.06 (1 H, s, H-5), 6.40 (1 H, d, *J* 0.5, H-3); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 31.00 (−, *Me*$_2$CO, solvated), 99.66 (−, C-5),

123.91 (−, C-3), 148.32 (+, C-4), 169.62 (+, C-2), 211.10 (+, Me_2CO, solvated); *m/z* 181/179 (M^+ + 1, 1%/8%), 180/178 (M^+, 19/23), 163/161 (6/7), 152/150 (8/9), 135/133 (7/8), 134/132 (95/100), 124/122 (3/3), 107/105 (13/14), 106/104 (25/26), 99 (29), 73 (8), 71 (6).

(5*S*)-4-Bromo-5-menthyloxyfuran-2(5*H*)-one 5

Mp 132 °C; $[\alpha]_{20}^{D}$ +26.6 (*c* 1.02 in $CHCl_3$); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.75–1.75 (16 H, m, H-menthyl), 2.20–2.48 (2 H, m, H-menthyl), 3.55 (1 H, dt, *J* 10/4, H-menthyloxy), 5.79 (1 H, d, *J* 1, H-5), 6.38 (1 H, d, *J* 1, H-3); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 15.83 (−, C-menthyl), 20.88 (−, C-menthyl), 22.11 (−, C-menthyl), 22.87 (+, C-menthyl), 25.15 (−, C-menthyl), 31.44 (−, C-menthyl), 34.10 (+, C-menthyl), 42.10 (+, C-menthyl), 48.04 (−, C-menthyl), 84.02 (−, C-menthyl), 104.84 (−, C-5), 124.15 (−, C-3), 146.15 (+, C-4), 168.00 (+, C-2) (Found: C, 53.04; H, 6.7. $C_{14}H_{21}BrO_3$ requires C, 53.15; H, 6.7%); IR, MS and HRMS data are consistent with those reported in the literature.[1]

X-Ray structure determination of compound 5

$C_{14}H_{21}BrO_3$, M = 317.22, monoclinic, space group $P2_1$ (No. 4), a = 8.292(1), b = 6.455(1), c = 14.465(2) Å, α = 90, β = 104.08(1), γ = 90°, V = 751.0(2) Å^3, Z = 2, D_c = 1.403 g cm^{-3}, F(000) = 328, crystal size 0.10 × 0.81 × 0.06 mm, T = 300 K, μ(Mo-Kα) = 27.4 cm^{-1}. Data collection: diffractometer Stoe IPDS (Imaging Plate), graphite-monochromated Mo-Kα radiation (fine-focus sealed tube, λ = 0.71073 Å), 2θ range = 5.0–48.2°, data set *h*, *k*, *l* −9: 9; −7: 7; −16: 16, total data 5435, unique data 2273, observed data 1868 with $I > 2\sigma(I)$, R_{int} = 0.032. Structure solution by SHELXS-86[13] and refinement by SHELXL-93,[14] hydrogen atoms in geometrically calculated positions, $\Delta\rho_{max}$ = 0.24 e Å^{-3}, $\Delta\rho_{min}$ = –0.25 e Å^{-3}, R (F^1) = 0.025 based on 1868 reflections with $F_o > 4\sigma(F_o)$, $wR2$ = 0.038, $wR2$ based on F^2 of 2273 reflections, Flack × parameter −0.00(1).

Minor diastereomer of 5

δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.75–1.75 (16 H, m, H-menthyl), 2.06–2.26 (2 H, m, H-menthyl), 3.65 (1 H, dt, *J* 10/4, H-menthyloxy), 5.88 (1 H, d, *J* 1, H-5), 6.37 (1 H, d, *J* 1, H-3); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 15.68 (−, C-menthyl), 20.83 (−, C-menthyl), 21.18 (−, C-menthyl), 23.03 (+, C-menthyl), 25.15 (−, C-menthyl), 31.55 (−, C-menthyl), 34.03 (+, C-menthyl), 40.30 (+, C-menthyl), 47.53 (−, C-menthyl), 80.50 (−, C-menthyl), 101.73 (−, C-5), 124.24 (−, C-3), 145.86 (+, C-4), 168.07 (+, C-2); IR, MS, HRMS data are consistent with those reported in the literature.[1]

(5*S*)-5-Menthyloxy-4-vinylfuran-2(5*H*)-one 6

A solution of (5*S*)-4-bromo-5-menthyloxyfuran-2(5*H*)-one **5** (3.17 g, 10 mmol) in THF (4 cm^3) was added dropwise to a suspension of $Pd(Ph_3P)_2Cl_2$ (350 mg, 5 mol%) in THF (6 cm^3) and acetonitrile (1 cm^3) under argon atmosphere. After stirring for 15 min at r.t. tributylvinylstannane (3.01 cm^3, 1.05 eq.) was added. The mixture was then stirred for two days at 35 °C. Evaporation of the solvent and column chromatography (silica gel, petroleum ether–diethyl ether 5:1) afforded (5*S*)-5-menthyloxy-4-vinylfuran-2(5*H*)-one **6** as white crystals (2.16 g, 8.17 mmol, 82%), mp 89 °C; $[\alpha]_{20}^{D}$ +37.03 (*c* 1.045 in $CHCl_3$); δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.75–1.17 (12 H, m, H-menthyl), 1.29–1.49 (2 H, m, H-menthyl), 1.63–1.72 (2 H, m, H-menthyl), 2.15–2.26 (1 H, m, H-menthyl), 2.30–2.38 (1 H, m, H-menthyl), 3.60 (1 H, dt, *J* 10.48/4.41, H-menthyloxy), 5.69 (1 H, d, *J* 11.03, H-2′), 5.81 (1 H, d, *J* 17.83, H-2′), 6.02 (2 H, m, H-3 and H-5), 6.55 (1 H, dd, *J* 17.83/11.03, H-1′); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 15.61 (−, C-menthyl), 20.92 (−, C-menthyl), 22.03 (−, C-menthyl), 22.60 (+, C-menthyl), 24.96 (−, C-menthyl), 31.49 (−, C-menthyl), 33.88 (+, C-menthyl), 42.29 (+, C-menthyl), 48.00 (−, C-menthyl), 82.33 (−, C-menthyloxy), 102.93 (−, C-5), 117.86 (−, C-3), 125.11 (+, C-2′), 126.94 (−, C-1′), 160.05 (+, C-4), 170.52 (+, C-2) (Found: C, 68.6; H, 4.1. $C_{16}H_{24}O_3$ requires C, 68.57; H, 4.03%); IR, MS and HRMS data are consistent with those reported in the literature.[1]

General procedure for the synthesis of *N*-(trimethylsilylmethyl)-benzylamines 8a–c

Benzylamine (1.5 eq.) **7a**–**c** was added to a suspension of anhydrous potassium carbonate (2.1 g, 0.5 eq.) in acetonitrile (60 cm^3). After stirring for 15 min at r.t. trimethylsilylmethyl chloride (4.2 cm^3, 30 mmol) was added over a period of 20 min. After being refluxed (4 d) the mixture was freed from solvent and purified by column filtration (silica gel, petroleum ether–diethyl ether 3:1) to give the monoalkylated products **8a**–**c**.

N-(Benzyl)trimethylsilylmethylamine 8a

The synthesis was performed according to the general procedure for the synthesis of *N*-(trimethylsilylmethyl)benzylamines to furnish a slightly yellow liquid (4.63 g, 24 mmol, 80%). The spectroscopic data are consistent with those reported in the literature.[6]

(1*R*)-*N*-(1-Phenylethyl)trimethylsilylmethylamine 8b. The synthesis was performed according to the general procedure for the synthesis of *N*-(trimethylsilylmethyl)benzylamines to give a colourless liquid (5.05 g, 24.4 mmol, 81%); δ_H(400 MHz; $CDCl_3$) 0.00 (9 H, m, $SiMe_3$), 1.30 (3 H, d, *J* 6.62, Me), 1.84 (1 H, d, *J* 13.61, CH_2SiMe_3), 1.92 (1 H, d, *J* 13.42, CH_2SiMe_3), 3.63 (1 H, q, *J* 6.62, PhCHMe), 7.13–7.35 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$) −2.66 (CH_3, $SiMe_3$), 24.38 (CH_3, Me), 37.90 (CH_2, CH_2SiMe_3), 62.11 (CH, PhCHMe), 126.61 (CH, Ph), 126.71 (CH, Ph), 128.25 (CH, Ph), 146.08 (C, Ph).

(1*S*)-*N*-(1-Phenylethyl)trimethylsilylmethylamine 8c

The synthesis was performed according to the general procedure for the synthesis of *N*-(trimethylsilylmethyl)benzylamines to furnish a slightly yellow liquid (4.65 g, 22.4 mmol, 75%); δ_C(100 MHz; DEPT; $CDCl_3$) −2.67 (CH_3, $SiMe_3$), 24.38 (CH_3, Me), 37.89 (CH_2, CH_2SiMe_3), 62.11 (CH, PhCHMe), 126.61 (CH, Ph), 126.70 (CH, Ph), 128.25 (CH, Ph), 146.06 (C, Ph); the proton NMR data are consistent with those reported in the literature.[7]

N-Benzyl-*N*-methoxymethyl(trimethylsilylmethyl)amine 9a

The synthesis was performed according to the literature.[6] Kugelrohr distillation (0.05 torr, bp 105 °C) gave a colourless liquid, yield 55%. Identified by spectral comparison.

(1*R*)-*N*-1-Phenylethyl-*N*-methoxymethyl(trimethylsilylmethyl)-amine 9b

The synthesis was performed according to the literature.[7] Kugelrohr distillation (0.05 torr, bp 115 °C) gave a colourless liquid, yield 64%; δ_C(100 MHz; DEPT; $CDCl_3$) −1.43 (CH_3, $SiMe_3$), 19.21 (CH_3, Me), 39.84 (CH_2, CH_2SiMe_3), 54.56 (CH_3, OMe), 61.77 (CH, PhCHMe), 85.82 (CH_2, CH_2OMe), 126.54 (CH, Ph), 127.45 (CH, Ph), 128.00 (CH, Ph), 145.23 (C, Ph); identified by spectral comparison.

(1*S*)-*N*-1-Phenylethyl-*N*-methoxymethyl(trimethylsilylmethyl)-amine 9c

The synthesis was performed according to the literature.[7] Kugelrohr distillation (0.05 torr, bp 115 °C) gave a colourless liquid, yield 69%. δ_C(100 MHz; DEPT; $CDCl_3$) −1.44 (CH_3, $SiMe_3$), 19.21 (CH_3, Me), 39.82 (CH_2, CH_2SiMe_3), 54.54 (CH_3, OMe), 61.77 (CH, PhCHMe), 85.80 (CH_2, CH_2OMe), 126.53 (CH, Ph), 127.43 (CH, Ph), 128.00 (CH, Ph), 145.22 (C, Ph); identified by spectral comparison of (1*R*)-enantiomer **9b**.

General procedure for the 1,3-dipolar cycloaddition

A flask containing 4-vinylfuranone **2** or **6** (1 mmol) and lithium fluoride (60 mg, 2.3 eq.) was evacuated and flushed several times with argon. A solution of *N*-benzyl-*N*-methoxymethyl-(trimethylsilylmethyl)amine **9a**–**c** (1.1 eq.) in acetonitrile (2.5 cm^3) was added at 0 °C. Then the mixture was sonicated for 8 h and stirred at −40 °C (addition of THF (1 cm^3) was necessary to maintain a liquid suspension) for several days. The reaction mixture was poured into water and extracted with diethyl ether (3 ×). The combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. The pyrrolidinyl-furanones were obtained after column chromatography.

4-(*N*-Benzylpyrrolidin-3-yl)furan-2(5*H*)-one 10. 4-Vinyl-furan-2(5*H*)-one **2** (110 mg, 1 mmol) was treated with *N*-benzyl-*N*-methoxymethyl(trimethylsilylmethyl)amine **9a** following the general procedure for the 1,3-dipolar cycloaddition to furnish pyrrolidinylfuranone **10** after chromatography (silica gel, gradient diethyl ether ⟶ diethyl ether–MeOH 10:1) as a yellowish viscous oil (163 mg, 0.670 mmol, 67%); $\nu_{max}(CHCl_3)$/cm^{-1} 2960, 2928, 2800, 1784, 1748, 1636, 1452, 1348, 1144, 1032, 892, 856; δ_H(200 MHz; $CDCl_3$; Me_4Si) 1.65–1.84 (1 H, m, H-4′), 2.10–2.32 (1 H, m, H-4′), 2.45–2.61 (2 H, m, H-5′), 2.63–2.82 (2 H, m, H-2′), 3.10–3.27 (1 H, m, H-3′), 3.56 (1 H, d, *J* 13, $PhCH_2$), 3.66 (1 H, d, *J* 13, $PhCH_2$), 4.75 (2 H, d, *J* 1.6, H-5), 5.79 (1 H, dt, *J* 1.6/1, H-3), 7.21–7.37 (5 H, m, Ph); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 29.93 (+, C-4′), 36.98 (−, C-3′), 53.13 (+, C-5′), 58.11 (+, C-2′), 59.70 (+, $PhCH_2$), 71.91 (+, C-5), 114.12 (−, C-3), 127.09 (−, Ph), 128.31 (−, Ph), 128.53 (−, Ph), 138.69 (+, Ph), 173.50 (+, C-4), 173.93 (+, C-2); *m*/*z* 244 (M^+ + 1, 5%), 243 (M^+, 28), 166 (6), 152 (4), 149 (4), 134 (6), 133 (24), 132 (11), 93 (10), 92 (13), 91 (100), 77 (6), 65 (18); *m*/*z* (M^+) found 243.1258; $C_{15}H_{17}NO_2$ requires 243.1259.

(5*S*)-4-(*N*-Benzylpyrrolidin-3-yl)-5-menthyloxyfuran-2(5*H*)-one 11a/12a. (5*S*)-5-Menthyloxy-4-vinylfuran-2(5*H*)-one **6** (222 mg, 0.840 mmol) was treated with *N*-benzyl-*N*-methoxymethyl-(trimethylsilylmethyl)amine **9a** following the general procedure for the 1,3-dipolar cycloaddition to furnish pyrrolidinyl-furanones **11a** and **12a** after chromatography (silica gel, diethyl ether–petroleum ether 1:1) as yellowish viscous oils (244 mg, 0.614 mmol, 73%, de 33%).

(5S)-4-[(3R)-N-Benzylpyrrolidin-3-yl]-5-menthyloxyfuran-2(5H)-one ***11a***. $\nu_{max}(CHCl_3)$/cm^{-1} 2960, 2924, 2872, 2800, 1793, 1756, 1648, 1452, 1368, 1332, 1256, 1240, 1128, 952, 904; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.63–1.50 (14 H, m, H-menthyl), 1.57–1.72 (2 H, m, H-menthyl), 1.82–2.02 (1 H, m, H-4′), 2.03–2.42 (2 + 1 H, m, H-menthyl and H-4′), 2.56–2.91 (4 H, H-2′ and H-5′), 3.02–3.21 (1 H, m, H-3′), 3.27–3.54 (1 H, m, H-menthyloxy), 3.60 (1 H, d, *J* 13.4, $PhCH_2$), 3.78 (1 H, d, *J* 13.4, $PhCH_2$), 5.68 (1 H, m, H-5), 5.90 (1 H, t, *J* 1, H-3), 7.20–7.41 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.57 (CH_3, C-menthyl), 21.02 (CH_3, C-menthyl), 22.10 (CH_3, C-menthyl), 22.67 (CH_2, C-menthyl), 25.29 (CH, C-menthyl), 29.30 (CH_2, C-4′), 31.63 (CH, C-menthyl), 34.01 (CH_2, C-menthyl), 36.27 (CH, C-3′), 42.39 (CH_2, C-menthyl), 48.15 (CH, C-menthyl), 53.29 (CH_2, C-5′), 58.25 (CH_2, C-2′), 60.04 (CH_2, $PhCH_2$), 83.33 (CH, C-menthyl), 104.63 (CH, C-5), 116.91 (CH, C-3), 127.16 (CH, Ph), 128.36 (CH, Ph), 128.62 (CH, Ph), 138.58 (C, C-4), 170.29 (C, C-Ph), 170.87 (C, C-2); *m*/*z* (110 °C) 397 (M^+, 2%), 396 (1), 313 (4), 269 (3), 259 (18), 258 (88), 242 (9), 241 (19), 213 (14), 168 (8), 150 (6), 133 (18), 105 (2), 91 (100), 83 (13), 69 (10); *m*/*z* (M − H^+) found 396.2539; $C_{25}H_{35}NO_3$ − 1 requires 396.2545.

(5S)-4-[(3S)-N-Benzylpyrrolidin-3-yl]-5-menthyloxyfuran-2(5H)-one ***12a***. $\nu_{max}(CHCl_3)$/cm^{-1} 2960, 2924, 2872, 2800, 1793, 1756, 1648, 1452, 1368, 1332, 1256, 1240, 1128, 952, 904; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.63–1.50 (14 H, m, H-menthyl), 1.57–1.72 (2 H, m, H-menthyl), 1.72–1.98 (1 H, m, H-4′), 2.03–2.42 (2+1 H, m, H-menthyl and H-4′), 2.56–2.91 (4 H, m, H-2′ and H-5′), 3.02–3.21 (1 H, m, H-3′), 3.27–3.54 (1 H, m, H-menthyloxy), 3.64 (2 H, m, $PhCH_2$), 5.75 (1 H, m, H-5), 5.83 (1 H, t, *J* 1, H-3), 7.20–7.41 (5 H, m, Ph); δ_C(50 MHz; APT; $CDCl_3$; Me_4Si) 15.71 (−, C-menthyl), 21.01 (−, C-menthyl), 22.13 (−, C-menthyl), 22.64 (+, C-menthyl), 25.31 (−, C-menthyl), 29.84 (+, C-4′), 31.55 (−, C-menthyl), 34.02 (+, C-menthyl), 35.85 (−, C-3′), 48.13 (−, C-menthyl), 53.35 (+, C-5′), 57.91 (+, C-2′), 59.96 (+, $PhCH_2$), 83.16 (−, C-menthyl), 104.48 (−, C-5), 116.29 (−, C-3), 127.08 (−, Ph), 128.29 (−, Ph), 128.58 (−, Ph), 138.59 (+, Ph), 170.44 (+, C-4), 170.74 (+, C-2); MS and HRMS: see (3*R*)-isomer.

(5*S*)-4-{(3*R* and 3*S*)-*N*-[(1*R*)-1-Phenylethyl]pyrrolidin-3-yl}-5-menthyloxyfuran-2(5*H*)-one 11b/12b. (5*S*)-5-Menthyloxy-4-vinylfuran-2(5*H*)-one **6** (200 mg, 0.757 mmol) was treated with (1*R*)-*N*-1-phenylethyl-*N*-methoxymethyl(trimethylsilylmethyl)-amine **9b** following the general procedure for the 1,3-dipolar cycloaddition to furnish pyrrolidinylfuranones **11b** and **12b** after chromatography (silica gel, diethyl ether–petroleum ether 1:2) as yellowish viscous oils (276 mg, 0.671 mmol, 88%, de 25%).

(5S)-{(3R)-N-[(1R)-1-Phenylethyl]pyrrolidin-3-yl}-5-menthyloxyfuran-2(5H)-one ***11b***. $[a]_{20}^{D}$ +25.27 (*c* 1.076 in $CHCl_3$); $\nu_{max}(CHCl_3)$/cm^{-1} 2960, 2920, 2872, 2796, 2360, 2340, 1760, 1648, 1452, 1376, 1328, 1228, 1128, 1096, 1048, 952; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.64–1.68 (16 H, m, H-menthyl), 1.37 (3 H, d, *J* 6.62, PhCHMe), 1.81–1.93 (1 H, m, H-4′), 2.06–2.10 (2 H, m, H-menthyl and H-4′), 2.04–2.31 (1 H, m, H-menthyl), 2.34 (1 H, dd, *J* 9.19/6.25, H-5′), 2.46–2.54 (1 H, m, H-5′), 2.69–2.77 (1 H, m, H-2′), 2.76–2.85 (1 H, m, H-2′), 3.02–3.12 (1 H, m, H-3′), 3.24 (1 H, q, *J* 6.62, PhCHMe), 3.41 (1 H, dt, *J* 10.66/4.23, H-menthyloxy), 5.65 (1 H, d, *J* 0.56, H-5), 5.88 (1 H, dd, *J* 1.47/0.92, H-3), 7.19–7.38 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.55 (CH_3, C-menthyl), 21.00 (CH_3, C-menthyl), 22.04 (CH_3, C-menthyl), 22.64 (CH_2, C-menthyl), 22.76 (CH_3, PhCHMe), 25.21 (CH, C-menthyl), 29.38 (CH_2, C-4′), 31.56 (CH, C-menthyl), 33.98 (CH_2, C-menthyl), 36.06 (CH, C-3′), 42.33 (CH_2, C-menthyl), 48.12 (CH, C-menthyl), 51.68 (CH2, C-5′), 57.11 (CH_2, C-2′), 65.21 (CH, C-menthyl), 83.18 (CH, PhCHMe), 104.75 (CH, C-5), 116.95 (CH, C-3), 126.92 (CH, Ph), 127.07 (CH, Ph), 128.37 (CH, Ph), 144.85 (C, Ph), 170.56 (C, C-4), 170.84 (C, C-2); *m*/*z* (140 °C) 412 (M^+ + 1, 1%), 411 (M^+, 4), 398 (4), 397 (27), 396 (M^+ − Me, 92), 334 (8), 272 (21), 258 (14), 220 (3), 196 (4), 168 (9), 152 (8), 124 (6), 106 (11), 105 (100), 91 (6), 83 (12), 69 (9); *m*/*z* (M^+) found 411.2773; $C_{26}H_{37}N_1O_3$ requires 411.2777.

(5S)-{(3S)-N-[(1R)-1-Phenylethyl]pyrrolidin-3-yl}-5-menthyloxyfuran-2(5H)-one ***12b***. δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.68–1.45 (14 H, m, H-menthyl), 1.39 (3 H, d, *J* 6.63, PhCHMe), 1.59–1.69 (2 H, m, H-menthyl), 2.08–2.23 (2 H, m, H-4′), 2.25–2.34 (2 H, m, H-menthyl), 2.43–2.54 (2 H, m, H-5′), 2.75–2.86 (2 H, m, H-2′), 3.02–3.13 (1 H, m, H-3′), 3.26 (q, *J* 6.63, PhCHMe), 3.50 (1 H, dt, *J* 10.66/4.23, H-menthyloxy), 5.74 (1 H, d, *J* 0.74, H-5), 5.87 (1 H, dd, *J* 1.47/0.92, H-3), 7.28–7.34 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.76 (CH_3, C-menthyl), 21.07 (CH_3, C-menthyl), 22.12 (CH_3, C-menthyl), 22.72 (CH_2, C-menthyl), 23.02 (CH_3, PhCHMe), 25.37 (CH, C-menthyl), 29.86 (CH_2, C-4′), 31.67 (CH, C-menthyl), 34.05 (CH_2, C-menthyl), 35.88 (CH, C-3′), 42.42 (CH_2, C-menthyl), 48.17 (CH, C-menthyl), 51.98 (CH_2, C-5′), 56.96 (CH_2, C-2′), 65.28 (CH, C-menthyl), 83.33 (CH, PhCHMe), 104.62 (CH, C-5), 116.60 (CH, C-3), 127.02 (CH, Ph), 127.12 (CH, Ph), 128.43 (CH, Ph), 144.98 (C, Ph), 170.47 (C, C-4), 170.95 (C, C-2); IR, MS and HRMS: see (3*R*)-isomer.

(5*S*)-{(3*R* and 3*S*)-*N*-[(1*S*)-1-Phenylethyl]pyrrolidin-3-yl}-5-menthyloxyfuran-2(5*H*)-one 11c/12c. (5*S*)-5-Menthyloxy-4-vinylfuran-2(5*H*)-one **6** (172 mg, 0.651 mmol) was treated with

(1*S*)-*N*-1-phenylethyl-*N*-methoxymethyl(trimethylsilylmethyl)-amine **9c** according to the general procedure for the 1,3-dipolar cycloaddition to furnish pyrrolidinylfuranones **11c** and **12c** after chromatography (silica gel, diethyl ether–petroleum ether 1:2) as yellowish viscous oils (185 mg, 0.450 mmol, 69%, de 41%).

(5S)-{(3R)-N-[(1S)-1-Phenylethyl]pyrrolidin-3-yl}-menthyloxyfuran-2(5H)-one ***11c***. $[\alpha]_{20}^{D}$ −19.72 (*c* 1.014 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 2960, 2928, 2872, 2792, 1800, 1756, 1648, 1492, 1452, 1368, 1328, 1236, 1132, 952, 908; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.60–1.43 (14 H, m, H-menthyl), 1.38 (3 H, d, *J* 6.62, PhCHMe), 1.55–1.68 (2 H, m, H-menthyl), 1.84–1.94 (1 H, m, H-4′), 2.00–2.14 (1 H, m, H-4′), 2.04–2.33 (3 H, m, 2 H-menthyl and H-5′), 2.45 (1 H, dt, *J* 9.01/6.8, H-5′), 2.70–3.00 (2 H, m, H-2′), 3.02–3.13 (1 H, m, H-3′), 3.23 (1 H, q, *J* 6.62, PhCHMe), 3.43 (1 H, dt, *J* 10.66/4.23, H-menthyloxy), 5.64 (1 H, m, H-5), 5.88 (1 H, dd, *J* 1.46/0.92, H-3), 7.20–7.37 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.45 (CH_3, C-menthyl), 20.96 (CH_3, C-menthyl), 22.06 (CH_3, C-menthyl), 22.64 (CH_2, C-menthyl), 22.98 (CH_3, PhCHMe), 25.25 (CH, C-menthyl), 28.81 (CH_2, C-4′), 31.59 (CH, C-menthyl), 33.99 (CH_2, C-menthyl), 36.22 (CH, C-3′), 42.39 (CH_2, C-menthyl), 48.13 (CH_2, C-5′), 57.42 (CH_2, C-2′), 65.33 (CH, C-menthyl), 83.26 (CH, PhCHMe), 104.75 (CH, C-5), 116.79 (CH, C-3), 126.92 (CH, Ph), 127.07 (CH, Ph), 128.41 (CH, Ph), 144.93 (C, Ph), 170.02 (C, C-4), 170.82 (C, C-2); *m/z* (120 °C) 411 (M^+, 2%), 397 (15), 396 (53), 333 (4), 272 (12), 257 (8), 2190 (25), 167 (4), 151 (4), 115 (19), 105 (10), 104 (100); *m/z* (M^+) found 411.2773; $C_{26}H_{37}N_1O_3$ requires 411.2753.

(5S)-{(3S)-N-[(1S)-1-Phenylethyl]pyrrolidin-3-yl}-5-menthyloxyfuran-2(5H)-one ***12c***. δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.67–1.45 (17 H, m, H-menthyl), 1.59–1.69 (2 H, m, H-menthyl), 2.07–2.34 (2 + 2 H, m, H-4′ + H-menthyl), 2.42–2.53 (2 H, m, H-5′), 2.68–2.90 (2 H, m, H-2′), 3.03–3.14 (1 H, m, H-3′), 3.20–3.34 (1 H, m, PhCHMe), 3.39–3.54 (1 H, m, H-menthyloxy), 5.76 (1 H, m, H-5), 5.81 (1 H, m, H-3), 7.18–7.38 (5 H, m, Ph); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.63 (CH_3, C-menthyl), 20.93 (CH_3, C-menthyl), 21.98 (CH_3, C-menthyl), 22.61 (CH_2, C-menthyl), 22.82 (CH_3, PhCHMe), 25.25 (CH, C-menthyl), 29.69 (CH_2, C-4′), 31.53 (CH, C-menthyl), 33.91 (CH_2, C-menthyl), 35.58 (CH, C-3′), 42.28 (CH_2, C-menthyl), 48.05 (CH, C-menthyl), 51.91 (CH_2, C-5′), 56.70 (CH_2, C-2′), 65.19 (CH, C-menthyl), 83.09 (CH, PhCHMe), 104.30 (CH, C-5), 116.12 (CH, C-3), 126.80 (CH, Ph), 127.07 (CH, Ph), 128.34 (CH, Ph), 144.67 (C, Ph), 170.53 (C, C-4), 170.77 (C, C-2); IR, MS and HRMS: see (3*R*)-isomer.

(5*S*)-5-Menthyloxy-4-[(2*S*)-oxiran-2-yl]furan-2(5*H*)-one 13

(5*S*)-5-Menthyloxy-4-vinylfuran-2(5*H*)-one **6** (1.06 g, 4 mmol) was dissolved in acetone (1 cm^3). Epoxidation was achieved by portionwise addition of a solution of dimethyldioxirane[15] in acetone (*ca*. 0.01 M, 1 eq./portion) until complete reaction (TLC monitoring) at r.t. Then the mixture was evaporated and purified by column chromatography on silica gel (petroleum ether–diethyl ether 10:1) to give the product as white-yellowish crystals (774 mg, 2.76 mmol, 69%, de 71%). Recrystallization from diethyl ether–petroleum ether afforded diastereomerically pure (5*S*)-5-menthyloxy-4-[(2*S*)-oxiran-2-yl]furan-2(5*H*)-one **13** as white crystals, mp 105 °C; $[\alpha]_{20}^{D}$ +81.81 (*c* 1.105 in $CHCl_3$); ν_{max}(KBr)/cm^{-1} 2984, 2920, 2864, 1788, 1760, 1652, 1456, 1332, 1256, 1124, 988, 960, 924, 888, 856; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.78–1.13 (12 H, m, H-menthyl), 1.23–1.50 (2 H, m, H-menthyl), 1.62–1.71 (2 H, m, H-menthyl), 2.08–2.20 (1 H, m, H-menthyl), 2.21–2.29 (1 H, m, H-menthyl), 3.02 (d, *J* 2.39) and 3.03 (d, *J* 2.58, 1 H, H-3′α), 3.10 (d, *J* 4.41) and 3.11 (d, *J* 4.23, 1 H, H-3′β), 3.57 (1 H, dt, *J* 10.66/4.41, H-menthyloxy), 3.71 (1 H, ddd, *J* 4.23/2.58/0.92, H-2′), 5.87 (1 H, d, *J* 1.1, H-5), 6.13 (1 H, t, *J* 0.92, H-3); δ_C(100 MHz; DEPT; $CDCl_3$; Me_4Si) 15.72 (CH_3, C-menthyl), 21.05 (CH_3, C-menthyl), 22.06 (CH_3, C-menthyl), 22.78 (CH_2, C-menthyl), 25.29 (CH, C-menthyl), 31.65 (CH, C-menthyl), 33.97 (CH_2, C-menthyl), 42.35 (CH_2, C-menthyl), 46.65 (CH, C-2′), 48.25 (CH, C-menthyl), 49.37 CH_2, C-3′), 82.87 (CH, C-menthyloxy), 102.75 (CH, C-5), 120.13 (CH, C-3), 163.11 (C, C-4), 169.60 (C, C-2); *m/z* (60 °C) 280 (M^+, 0%), 249 (2), 195 (7), 155 (4), 138 (70), 125 ($M^+ - C_{10}H_{19}O$, 62), 123 (18), 109 (10), 97 (22), 95 (59), 84 (34), 81 (100), 69 (66), 67 (20); *m/z* (M^+) found 280.1675; $C_{16}H_{24}O_4$ requires 280.1659 (Found: C, 62.85; H, 3.7. $C_{16}H_{24}O_4$ requires C, 62.83; H, 3.69%).

X-Ray structure determination of compound 13

$C_{16}H_{24}O_4$, $M = 280.36$, monoclinic, space group $P2_1$ (No.4), $a = 8.421(2)$, $b = 6.173(1)$, $c = 15.251(2)$ Å, $\alpha = 90$, $\beta = 94.28(2)$, $\gamma = 90°$, $V = 790.6(3)$ $Å^3$, $Z = 2$, D_c 1.178 g cm^3, $F(000) = 304$, $T = 300$ K, μ(Mo-Kα) = 0.8 cm^{-1}, crystal size 0.33 × 1.44 × 0.22 mm. Data collection: diffractometer Stoe IPDS (Imaging Plate), graphite-monochromated Mo-Kα radiation (fine-focus sealed tube, $\lambda = 0.71073$ Å), 2θ range = 5.3–48.1°, scan type = 150 imaging plates, $\Delta\varphi = 1.5°$, data set *h*, *k*, *l* −9: 9; −6: 6; −17: 17, total data 5638, unique data 2371, $R_{int} = 0.025$, observed data 1817 with $I > 2\sigma(I)$. Structure solution by SHELXS-86, refinement by SHELXL-93, hydrogen atoms in geometrically calculated positions, $\Delta\rho_{max} = 0.07$ e $Å^{-3}$, $\Delta\rho_{min} = -0.06$ e $Å^{-3}$, $R(F) = 0.0268$ based on 1817 reflections with $F_o > 4\sigma(F_o)$, $wR2 = 0.0485$, $wR2$ based on F^2 of 2371 reflections.

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